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SYNTHESIS OF HEAT-RESISTANT GLASS CRYSTAL COATINGS USING HIGH-ALUMINA WASTE

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The results of synthesis and physical-chemical investigations of heat-resistant glass ceramic coatings, which are intended for use as high-temperature corrosion protection for nichrome alloys, using high-alumina waste from the metallurgical industry are presented. The mechanism of sitallization of the glass matrix of the coating as well as the phase composition of the heat-resistant coatings and the nichrome – coating contact layers are determined as functions of the ratio of the bonding activators — NiO and CoO.

Resource conservation is now of great importance. This is because new scientific ideas are being used to intensify technologies. The development and practical use of materials with complex, prescribed, physical – chemical and mechanical properties, intended to protect various metals, specifically, nichrome steels and alloys, from corrosive media is an urgent problem whose solution will make it possible to obtain new heat-resistant and chemically stable structural materials.

It is known that an effective method of protecting chromium steels and alloys from high-temperature corrosion is to apply a coating with a sitallic structure [1, 2]. Such coatings possess a wide spectrum of properties: they protect metal from high-temperature gas corrosion and damage in metal melts and they possess high thermostability, heat-insulating action, and other properties. In addition, sitallic coatings promote retention of the mechanical strength of alloys and prolong the service life of structures. However, there are comparatively few works on the use of technogenic materials in the field of heat-resistant glass crystal coatings. Thus it is useful to study the possibility of replacing chemically pure components of a coating by technogenic initial material. This permits solving two problems — economic and ecological, which will decrease the consumption of raw materials and permit recycling various industrial wastes.

We investigated metallurgical wastes, specifically, alumina-containing wastes (ACW), as a basis for developing heat-resistant coatings which would protect nichrome steels and alloys from high-temperature corrosion.

The nichrome alloys Kh20N80 and KhN78T in the form of slabs ($20 \times 8 \times 2$ m) were used as samples for depositing coatings for commercial tests as well as for laboratory investigations. The nichrome samples were subjected to preliminary mechanical, thermal, and chemical treatment.

Together with the preparation of nichrome, we prepared enamel slip, which comprised a colloidal-disperse system of a finely disperse powder of a glass matrix (No. 0063 sieve), distilled water, and additives.

The glass-forming composition was chosen on the basis of the system $R_xO_y - Al_2O_3 - SiO_2 - TiO_2$ (R — Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, Mn^{4+}) with no more than 50%[2] SiO_2 in order to prevent undesirable structural changes in the main crystalline phases of the glass matrices and coatings.

ACW from the Belokalitvenskii Metallurgical Works were introduced into the mix instead of commercial grade alumina. X-ray phase analysis performed at the Regional Laboratory Center "Yuzhgeoligiya" showed that the wastes had been checked for radioactivity and toxicity. The results satisfy existing sanitary norms.

X-ray phase analysis showed that the ACW mainly contain free aluminum oxide γ-$Al_2O_3 \cdot H_2O$ in the form of boehmite (85% Al_3O_3 and 15% H_2O). An irreversible transition in γ-Al_2O_3 (alumina) occurs during heat treatment:

$$\gamma\text{-}Al_2O_3 \cdot H_2O \xrightarrow{490 - 550°C} \gamma\text{-}Al_2O_3.$$

The chemical composition of ACW is as follows (%): 12.93 SiO_2, 76.94 Al_2O_3, 2.08 Fe_2O_3, 0.34 TiO_2, 0.04 Cr_2O_3, 0.05 MnO_2, 1.89 CaO, 1.65 MgO, 2.37 K_2O, 1.67 Na_2O, 0.03 MoO_3, and 0.01 Sb_2O_3.

Of no small importance is the presence in ACW of Fe_2O_3, Cr_2O_3, and MnO_2, which affect the wetting power and

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[2] Here and below — content by weight.

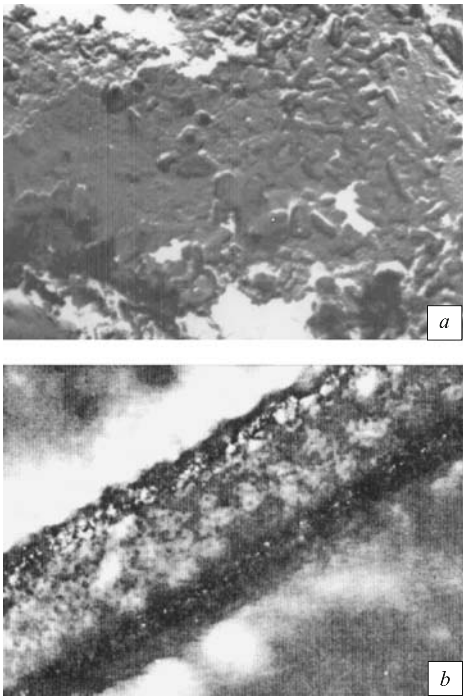

Fig. 1. Microstructure (× 10000) of a coating (*a*) and nichrome – coating contact layer (*b*).

bonding of nichrome and the coating, as well as of the surface-active oxides MoO_3 and Sb_2O_3, which even in negligible quantities have a large effect on the surface tension of coating melts.

Eight compositions for glass matrices were determined for the purpose of developing a composition of a glass matrix of a heat-resistant glass crystal coating. These compositions differed by the additions of oxides of a complex catalyst, containing primarily TiO_2 and ZnO, as well as oxides present in ACW. The glasses were synthesized at temperature 1350 – 1400°C with holding time 1 – 3 h.

The crystallizability of the glass matrices of the coatings was studied by polythermal and differential-thermal analysis. The glass samples were place in alundum crucibles in a furnace and held for 1 h in the temperature interval 500 – 800°C. It was determined that conditionally complete volume crystallization in glass with the optimal composition occurs in the temperature interval 600 – 800°C with the ratios $Li_2O : ZnO : TiO_2 = 7.3 : 5.0 : 6.3$. DTA showed that the main exothermal effects are observed at 730 and 780°C, and pre-crystallization processes occur in the temperature interval 520 – 600°C. It was determined that the optimal regime for sitallization of the glass matrix of the coating is heat-treatment in two stages: $t_1 = 520°C$, $t_2 = 780°C$; $\tau_1 = \tau_2 = 1$ h.

To study the phase composition the samples of the glass matrix of the coating, which were heat-treated in accordance with the sitallization regime, were cooled and then examined in an electron microscope and subjected to x-ray phase analysis. The electron-microscope analysis of the heat-treated samples of the glass matrix made it possible to conclude the following: the size of these crystalline particles ranges from 500 to 1000 nm, which attests to the formation of a sitallic structure in the experimental glass matrix.

TABLE 1.

Coating	Bonding oxides content, wt.%	
	NiO	CoO
1	1	2
2	2	1
3	3	0

The physical – chemical properties of a glass matrix with optimal composition were determined: CLTE — $115 \times 10^{-7} K^{-1}$, softening temperature — 660°C; density before heat-treatment — 2500 kg/m^3; density after heat treatment in the range 520 – 950°C increased substantially to 2880 kg/m^3, which corresponds to the requirements for the glass matrix of heat-resistance coatings.

A slip with the following composition was prepared to develop and investigate coatings (%): 97 glass matrix (frit); 0 – 3 NiO and CoO as bonding activators; 5.0 (above 100%) of Vladimirovskoe clay and 0.1 (above 100%) H_3BO_3. Water was used as the dispersion medium. The moisture content of the coating slips was 40 – 45%.

A brush and immersion were used to deposit on nicrome the slip prepared for the heat-resistant coating, after which the samples were allowed to dry completely. The optimal firing regime for the coatings was determined — temperature 1150°C; holding time 3 min.

Three coating compositions with different content of the bonding oxides were prepared on the basis of the glass matrix with optimal composition (see Table 1).

The physical – chemical and utilization properties of the synthesized coatings were studied to determine the optimal ratio of the bonding activator oxides (NiO and CoO) in the coatings. The coating 2 possesses the highest CLTE ($130 \times 10^{-7} K^{-1}$). This CLTE differs from that of the nichrome alloy Kh20N80 by only $25 \times 10^{-7} K^{-1}$, which is what predetermines the required bonding strength. The dark-green coatings with subdued luster have quite high thermomechanical properties. The coating 2 possesses the greatest heat-resistance: by 28 and 38 heat cycles higher than that of coatings 1 and 3, respectively.

The mass change of the samples as a function of the holding time at 1000°C was used to judge the heat-resistance of the coatings. The tests were performed over a period of 100 h under laboratory conditions. After 50 h of cyclic tests of samples which were not heat-treated it was determined that the coatings 1 and 2 decrease the corrosion of Kh20N80 alloy by the factors 1.32 and 1.54, respectively.

The coatings were heat-treated in two steps according to the sitallization regime of the glass matrix: $t_1 = 520°C$,

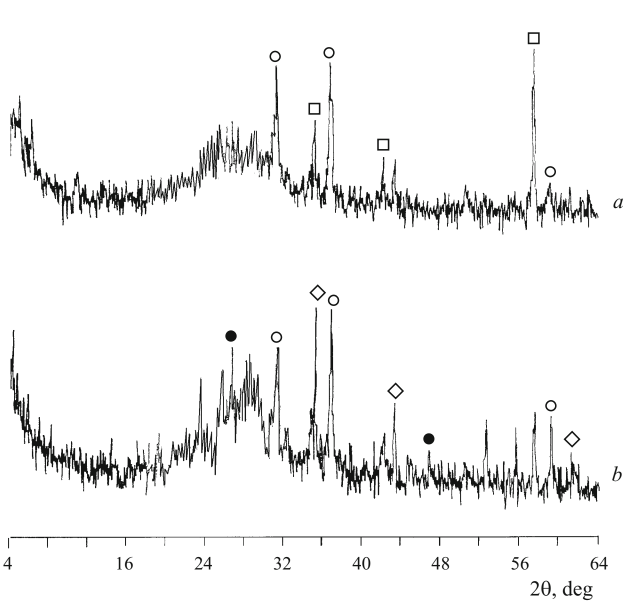

Fig. 2. X-ray diffraction patterns of the coatings: *a*) coating 2: ○) $ZnAl_2O_4$ (gahnite), □) tial Al_2TiO_5; *b*) coating 1: ○) $Ca_2ZnSi_2O_7$ (hardystonite), ◇) $MgTi_2O_5$ (magnesium titanate), ●) $CaAl_2Si_2O_8$ (anortite).

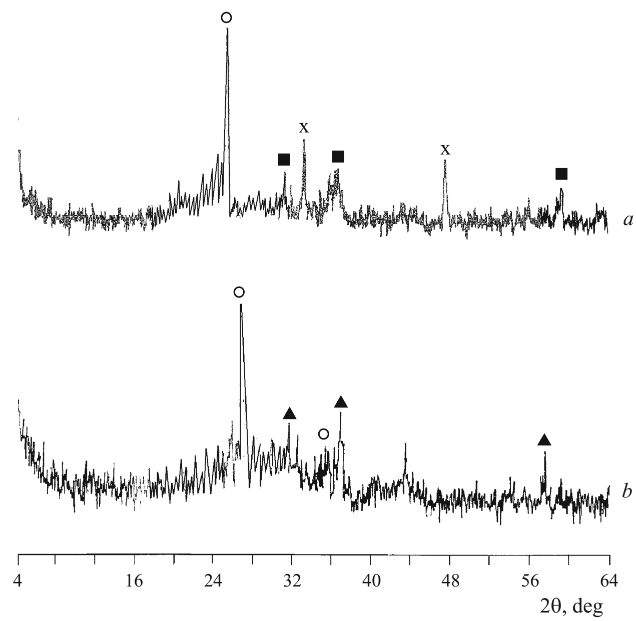

Fig. 3. Nichrome – coating contact layer: *a*) coating 2: ○) $MgTi_2O_5$, ■) $MgCr_2O_4$ (magnesiochromite), ×) $ZnSiO_4$ (willemite); *b*) coating 1: ○) $MgTi_2O_5$, ▲) $Ca_3Si_3O_9$.

$t_2 = 780°C$; $\tau_1 = \tau_2 = 2$ h. As a result, the weight increment of the samples decreases as follows: after 50 h by a factor of 2.3 with coating 1 and a factor of 2.5 with coating 2.

The composition dependence of the bonding strength of a coating was determined by a rapid method that makes it possible to test the bonding strength of a coating on nichrome by bending the sample by 180°. After bending, the bonding strength was evaluated as a percentage of cleavages in the coating per unit surface area. It was determined that the bonding strength of all coatings is 5 units, since the area of a cleavage of the coatings does not exceed 1% in each case.

Electron microscopy and x-ray phase analysis were used to determine the phase composition and the structure of the coatings and the contact layers in the nichrome – coating system.

The crystalline particles of the crystal glass materials obtained ranged in size from 500 to 1000 nm (Fig. 1). This attests to the formation of a sital structure in the coatings investigated.

For coating 2 diffraction peaks were found at 0.160, 0.218, and 0.254 nm due to tial Al_2TiO_5 and at 0.155, 0.243, and 0.286 nm due to $ZnAl_2O_4$ (gahnite), which belongs to the cubic system, which in turn gives a closer packing of the atoms (Fig. 2). In addition, gahnite possesses high density — 4600 kg/m^3 and hardness — 7.5 – 8.0 as well as a high melting temperature — 1930°C, which gives the coating high heat-resistance. In coating 1 the Al_2TiO_5 phase is absent and anortite $CaAl_2Si_2O_8$ (0.193, 0.334, 0.379 nm) and magnesium titanate $MgTi_2O_5$ (0.151, 0.200, 0.255 nm) as well as hardystonite $Ca_2ZnSi_2O_7$ (0.156, 0.244, 0.286 nm) were found. In addition to the crystalline phases that were found, the coating samples contain a residual glass phase.

X-ray phase analysis also revealed a difference between the phase compositions of the contact layers with nichrome alloy. The x-ray diffraction pattern of the contact layer for coating 2 with nichrome (Fig. 3) makes it possible to establish the presence of the following phases: $MgTi_2O_5$ (0.3528 nm), $ZnSiO_4$ – willemite (0.1912, 0.2708, 0.4175 nm), and spinel $MgCr_2O_4$ – magnesiochromite (0.1560, 0.2476, 0.2870 nm). The following crystalline phases were determined in the contact layer of coating 1: $Ca_3Si_3O_9$ (0.2552, 0.3366, 0.3474 nm), $MgTi_2O_5$ (0.1604, 0.2450, 0.2838 nm). This explains the negligible difference in the bonding strength and service life of the experimental coatings.

In summary, coating 2, containing a glass matrix with the optimal composition based on the system $R_xO_y – Al_2O_3 – SiO_2 – TiO_2$ and NiO and CoO in the ratio NiO : CoO = 2 : 1 as the bonding activators, provides effective high-temperature corrosion protection for the nichrome alloy Kh20N80.

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